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INTERFACES OF HIGH-PROTECTION PERFORMANCE POLYARYLS-COATED ZINC PHOSPHATED STEELS

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P P E E K

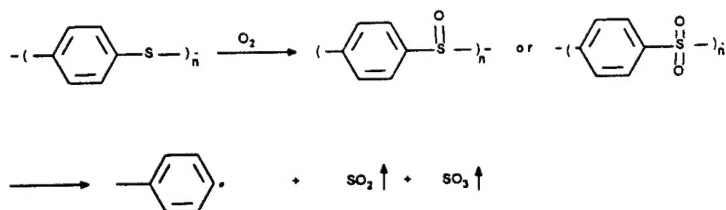
Abstract

To evaluate the ability of polyaryl thermoplastic coatings such as polyphenylenesulfide (PPS) and polyphenyletheretherketone (PEEK), to protect zinc phosphate (Zn·Ph)-treated steels from corrosion in a wet, harsh environment (1.0 wt% H₂SO₄, 3.0 wt% NaCl and 96.0 wt% water at temperature from 25° to 200°C), we exposed them in autoclave to measure their performance in heating-cooling cyclic fatigue tests (1 cycle = 12 hr at 200°C + 12 hr at 25°C) for up to 90 cycles. Although no changes in appearance were seen in the PEEK specimens after 60 cycles, extension to 90 cycles caused delamination of the coating film from the Zn·Ph; the major reason was the degradation of the PEEK polymer caused by its hydrothermal-catalyzed esterification. In urea hydrogen peroxide (UHP) modified PPS-coating systems, chemical reactions at the interfaces between the PPS and Zn in the Zn·Ph layer led to the formation of a ZnS reaction product, which enhanced the Zn·Ph-to-PPS adhesive bond; correspondingly, there were no signs of peeling nor separation of the coating after 90 cycles. In addition, because these intermediate reaction products are insoluble at high pH, they minimized the rate of delamination of the PPS coating caused by the cathodic reaction, $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$, at the corrosion side of a defect in the film. In contrast, PEEK coatings containing non-reactive Zn·Ph underwent cathodic delamination because of the susceptibility of Zn·Ph to alkali dissolution.

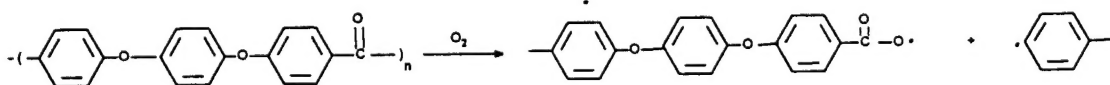
Introduction

Semi-crystalline polyphenyletheretherketone (PEEK) and polyphenylenesulfide (PPS) thermoplastics are very attractive for application as corrosion-protective coatings of cold-rolled steels in harsh environments at hydrothermal temperatures up to 200°C. The major characteristic of these linear polyaryls is the molecular orientation caused by the chain extension at their melting point, ~

290°C for PPS^{1,2}, and $\approx 340^\circ\text{C}$ for PEEK^{3,4}. This orientation leads to the crystallization of these polymers during cooling. Such melt-crystallization behavior of these polyaryls give them specific, desirable characteristics as coatings; they show high-temperature stability, chemical and hydrothermal resistance, and have good mechanical properties. In addition, there are no limitations on their shelf- or pot-life, nor problems of waste disposal because any excess crystallized polyaryl phase reverts to the molten phase in a hot oven. Also, the surfaces of powdered form of these polyaryls have a good wettability in water, suggesting that the water-based polymer slurries can be formulated to use in simple dip-withdrawing and cold spray coating methods. In a previous study^{5,6}, we investigated the interface of polyaryls-to-steel joints prepared in oxygen or nitrogen environments at $\approx 350^\circ\text{C}$. With PPS, its oxidation reaction in hot O_2 caused the emission of corrosive reactants, such as SO_2 and SO_3 gases, in accordance with following O_2 -associated degradation routes;



The interfacial interaction of these gases with Fe_2O_3 at the outermost surface side of steel introduced sulfur-related reaction products, such as $\text{Fe}_2(\text{SO}_4)_3$, FeSO_4 , and FeS , into the critical interfacial boundary zones. However, although these reaction compounds are known as the corrosion products of steel, they significantly improved the bond strength between the PPS and steel. In contrast, the adherence of PPS prepared in hot N_2 to steel was very poor. In the PEEK/steel joint systems, the O_2 -catalyzed degradation of PEEK promoted the incorporation of carboxylate groups into the chain-scissored linear structure;



Such degradation not only corresponded to a low degree of crystallinity of PEEK, but also caused its separation from the steel. A good adhesion performance of PEEK to steel was noted in the joint specimens prepared in a N_2 .

We also searched the rate of cathodic delamination of polyaryl films from steel, brought about by the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, which occurs under the coating adjacent to the

defect^{7,8}. A considerable attention in this corrosion reaction processes was given to the creation of a high pH environment at the cathodic sites; namely, the created alkali circumstance beneath the coating not only causes the formation of corrosion products, but also promoted the alkali-catalyzed decomposition of the interfacial reaction products, especially for $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 , at the PPS/steel interfaces, and the saponification of the PEEK polymer in contact with the steel. Subsequently, these phenomena led to a high rate of cathodic delamination of the polyaryl films from the steels. Thus, the necessity of the interface tailoring and modification to inhibit the onset of the cathodic reaction and to avoid the direct contact of polyaryl with steel becomes a more important subject. Regarding the interfacial tailoring material systems, the introduction of zinc or zinc alloy and zinc phosphate ($\text{Zn}\cdot\text{Ph}$) conversion coatings into the intermediate layers is widely employed as a post-treatment of steel surfaces in the autobody industry.

On the basis of this information, an emphasis in this present work was directed toward exploring the changes in chemistry and morphology occurring at the interfaces between peroxide modified PPS or unmodified PEEK coatings and phosphated steels after heating-cooling cycle fatigue tests of the defect-free polyaryl topcoat/ $\text{Zn}\cdot\text{Ph}$ /steel systems in an accelerated corrosion environment at 25° to 200°C.

Materials

PPS and PEEK powders for the slurry coatings were supplied by the Phillips 66 Company and the Imperial Chemical Industry (ICI), respectively. The urea hydrogen peroxide (UHP) received from Aldrich was used as the peroxidic reagent which promote the rate of oxidation of sulfur in the PPS. These polyaryl films were deposited on the surfaces of the $\text{Zn}\cdot\text{Ph}$ -treated steel substrate in the following way. First, the substrates were dipped into the polyaryl slurries (see Table 1) at 25°C. The PPS slurry-coated substrates were heated in air for 2 hrs at 350°C; and the PEEK slurry-coated substrates were heated in N_2 for 2 hrs at 400°C, and then cooled to room temperature at the rate of - 10°C/min. The thickness of the polyaryl coating films of all specimens ranged from 0.075 to 0.1 mm.

Table 1
Formulation of UHP-Modified and Unmodified PPS and PEEK Slurries

<u>Polyaryl</u>	<u>Slurry formulation</u>
PEEK	40 wt% PEEK-52 wt% water-8 wt% propyleneglycol
PPS	40 wt% PPS-52 wt% water-8 wt% propyleneglycol
PPS	39 wt% PPS-50 wt% water-8 wt% propyleneglycol-3 Wt%UHP
PPS	37 wt% PPS-48 wt% water-8 wt% propyleneglycol-7 wt%UHP

Measurements

The cyclic fatigue tests for the PPS and PEEK-coated Zn·Ph steel panels (7.5 cm x 7.5 cm) were accomplished as follows; the coated specimens were directly soaked in a corrosive solution consisting of 1.0 wt% H₂SO₄, 3.0 wt% NaCl, and 96.0 wt% water at temperatures from 25 to 200°C, and then the heating-cooling cycles (one cycle = 12 hrs at 200°C + 12 hrs at 25°C) were repeated up to 90 times. The overall appearance and the interfaces of the specimens after 1, 5, 10, 20, 30, 60, and 90 cycles were examined to gain the information on their hydrothermal durability or the decomposition of coatings, and the changes in chemical nature occurring at the polymer-substrate interfaces. These information were gained using the combined technologies of scanning electron microscopy (SEM), energy-dispersion x-ray spectrometry (EDX), and x-ray photoelectron spectroscopy (XPS). The integrated data from all these approaches were correlated directly with the corrosion-related data, such as the impedance, |Z|, obtained from AC electrochemical impedance spectroscopy (EIS) in an aerated 0.5 N NaCl electrolyte at 25°C, and also cathodic delamination tests. The latter were conducted in an air-covered 1.0 M NaCl solution using an applied potential of - 1.5 V vs. SCE for 8 days. The total area of film in contact with the NaCl solution was 6.0 x 10³ mm². A defect was made using a 1-mm diameter drill bit. After exposure, specimens were removed from the cell and allowed to dry. The polyaryl coating was removed by cutting, revealing a delaminated region that appeared as a light gray area adjacent to the defect.

Results and Discussion

Table 2 shows the changes in appearance of coatings for the PEEK/Zn·Ph/steel, and the UHP-modified and unmodified PPS/steel and /Zn·Ph/steel joint systems as a function of cycle number. Using PEEK

Table 2
Visual Observation of PPS and PEEK Coating Films as a Function of Heating-Cooling Cycles

<u>Polymer</u>	<u>Substrate</u>	UHP %	Cycles					
			<u>1</u>	<u>5</u>	<u>10</u>	<u>30</u>	<u>60</u>	<u>90</u>
PEEK	Zn·Ph/steel	0	good	good	good	good	good	peels
PPS	steel	0	peels	-	-	-	-	-
PPS	steel	3	good	peels	-	-	-	-
PPS	steel	7	good	blister	peels	-	-	-
PPS	Zn·Ph/steel	0	good	good	good	good	good	good
PPS	Zn·Ph/steel	3	good	good	good	good	good	good
PPS	Zn·Ph/steel	7	good	good	good	good	good	good

coating, no blistering and lifting in appearance were observed in the specimens after 60 cycles; however, an increase to 90 cycles caused the peeling of the film from the Zn·Ph. Rust stains were clearly seen on the separated substrate surfaces. When the PPS coating was deposited directly to the steel surfaces in the absence of Zn·Ph, the durability of the bond between the coating and the steel depended on the concentration of UHP. The incorporation of 3 wt% UHP into the PPS gave a better performance; peeling of the film occurred after 5 cycles, compared with only one cycle for film without UHP. A further increase in concentration of UHP to 7 wt% extended the service life to 10 cycles. An encouraging result was obtained from cyclic tests of all the PPS-coated zinc phosphated steel specimens; there are no visual signs of delamination and damage after 90 cycles in either the modified and unmodified coating films. This result proved that the bond durability at the interfaces between PPS and Zn·Ph is outstanding, even in such a harsh environment.

To establish the interfacial bond structure and chemical states that govern such poor and good bond durability of polyaryl coatings, we investigated the interfacial polyaryl coating and Zn·Ph sides of the PEEK/ and PPS/Zn·Ph/steel joints before and after 90 cycles by XPS. The XPS C_{1s} core-level spectra of the PEEK side separated from the phosphated steel before and after 90 cycles were illustrated in Figure 1. The C_{1s} region of uncycled PEEK side can be deconvoluted by four resolvable Gaussian components at BEs of 285.0 eV, 286.5 eV, 288.0 eV, and 291.5 eV. All these components correspond to the structure of PEEK itself. A striking difference in spectral features was observed from the PEEK interface after 90 cycles; the width of the overall peak from 282 to 290 eV was more extensive, suggesting that an additional chemical component was introduced into the interfacial PEEK side during the fatigue tests. The new component, which is reflected in peak No. 5 at 289.4 eV, can be ascribed to the formation of -COO- (carboxylic acid or ester) groups. Such an additional component clearly verified that the PEEK coating itself undergoes hydrothermal-catalyzed esterification. Thus, a high susceptibility of PEEK to hydrothermal-catalyzed esterification causes the degradation of the polymer film, thereby resulting in its delamination.

In the 0, 3, and 7 wt% UHP-modified PPS/Zn·Ph/steel joint systems, the $Zn_{2p_{3/2}}$ spectra for the interfacial Zn·Ph side of uncycled specimens are depicted in Figure 2. The spectrum of the control (0 wt% UHP) reveals only a single symmetric peak at 1024.6 eV, caused by Zn originating from the Zn·Ph. A noticeable change in the shape of the $Zn_{2p_{3/2}}$ signal from the 3 wt% UHP specimen was the emergence of a new signal at 1022.7 eV, corresponding to the Zn in the ZnS reaction product derived from the interaction between PPS and Zn·Ph; the intensity of this peak grew with the increasing concentration of UHP. At 7 wt% UHP, the peak at 1022.7 eV becomes the dominant component, while the Zn·Ph-related peak at 1024.6 eV

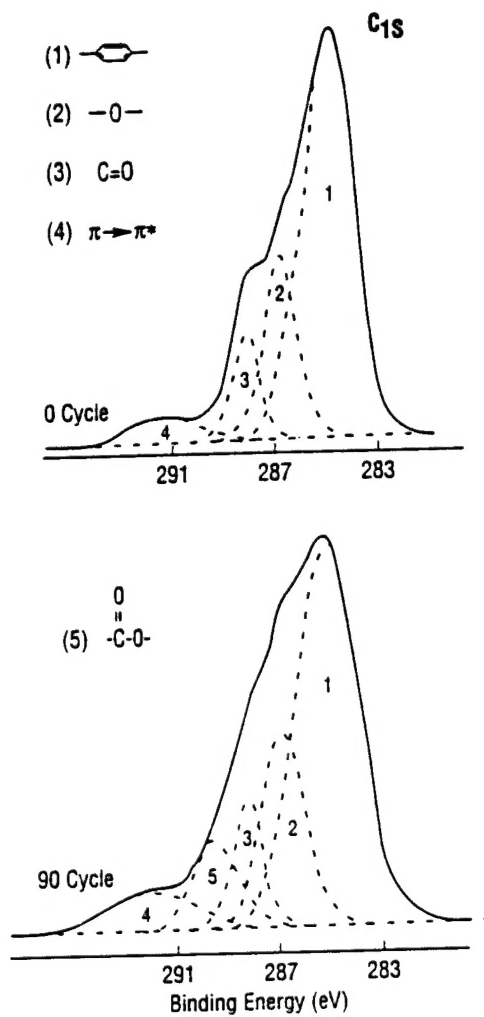


Figure 1. XPS C_{1s} core-level spectra for interfacial PEEK sides before (0 cycle) and after 90 cyclic tests.

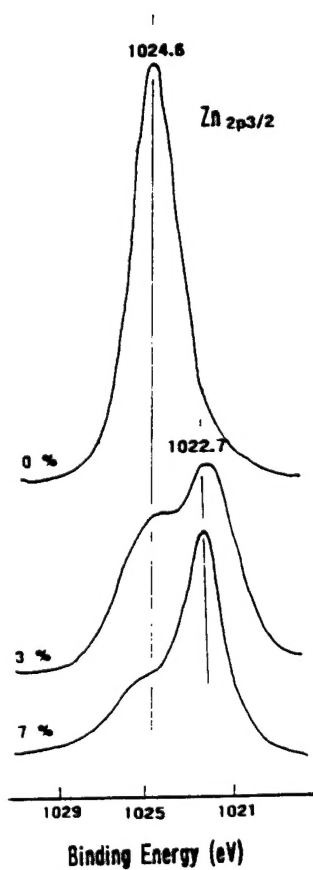


Figure 2. $\text{Zn}_{2p_{3/2}}$ region of interfacial $\text{Zn} \cdot \text{Ph}$ sides removed from the 0, 3, and 7 wt% UHP-modified PPS before cyclic tests.

considerably decays. We note that there were no signals reflecting zinc sulfite (ZnSO_3) or sulfate (ZnSO_4) compounds. Hence, it is possible to assume that the peroxidic reaction of PPS with UHP emits SO_2 or SO_3 gases adjacent to the Zn·Ph layers, and then the emitted gases favorably react with the Zn in Zn·Ph to form ZnS. If this interpretation is correct, a high rate of peroxidic reaction increasingly promotes the transformation of anhydrous α - and γ - $\text{Zn}_3(\text{PO}_4)_2$, as the major phases of Zn·Ph, into ZnS. For more interesting, we found that although UHP-unmodified PPS was used, ZnS also forms at interfaces between the PPS and the Zn·Ph during the cyclic tests. Figure 3 displays the changes in spectral features in

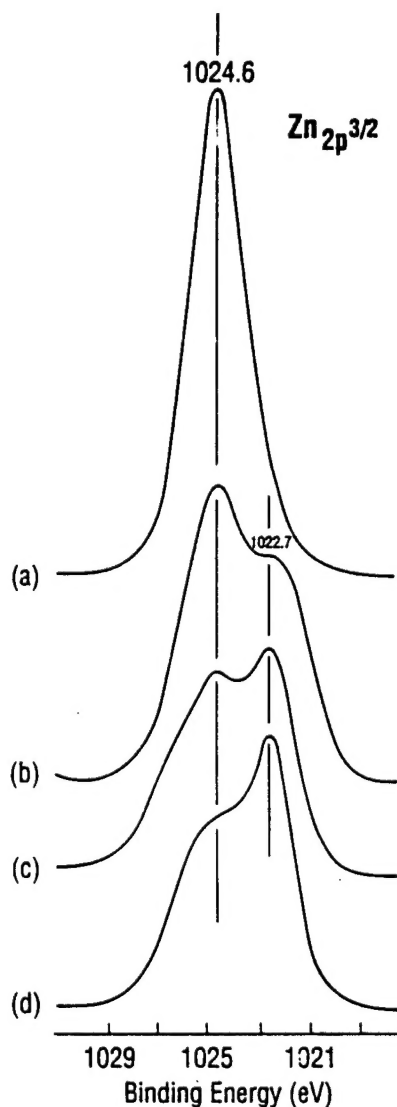


Figure 3. $\text{Zn}_{2p^{3/2}}$ region of the Zn·Ph interface of 0(a)-, 30(b)-, 60(c)-, and 90(d)-cycled specimens.

the $\text{Zn}_{2\text{P}_{3/2}}$ region of the $\text{Zn}\cdot\text{Ph}$ side removed from the unmodified PPS as a function of cycle number. The data clearly verified that the line intensity of the signal at 1022.7 eV, corresponding to ZnS , grew with the increase in the number of cycles, while the peak line of $\text{Zn}\cdot\text{Ph}$ at 1024.6 eV conspicuously attenuated. It is apparent that the ZnS reaction product formed at the PPS- $\text{Zn}\cdot\text{Ph}$ contact zones plays a major role in forming an intermediate cross-linking structure, which improves the $\text{Zn}\cdot\text{Ph}$ -to-PPS adhesive forces.

All this information was correlated directly with the results from electrochemical impedance spectroscopy (EIS) and cathodic delamination tests of the uncycled and cycled polaryl-coated $\text{Zn}\cdot\text{Ph}$ specimens. Figure 4 shows the changes in impedance, $|Z|$, at 0.01 Hz for these coatings as a function of cycle number. For the uncycled

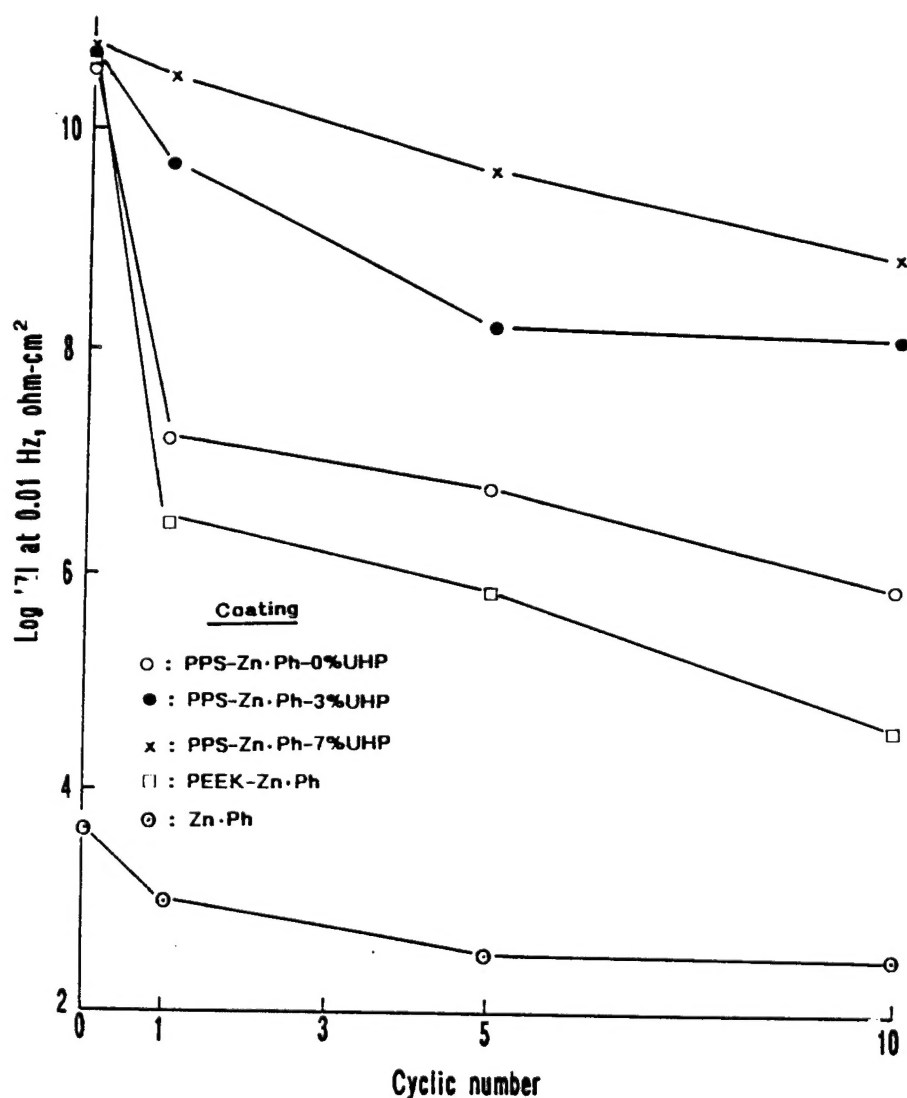


Figure 4. Changes in impedance, $|Z|$, for UHP-modified and unmodified PPS/ $\text{Zn}\cdot\text{Ph}$, and unmodified PEEK/ $\text{Zn}\cdot\text{Ph}$ and single $\text{Zn}\cdot\text{Ph}$ systems as a function of cycle number.

specimens, the impedance of Zn·Ph-coated steel in the absence of the polyaryls was $\sim 7.0 \times 10^3$ ohm-cm². Once the Zn·Ph surfaces were coated with the polyaryls, the IZl value increased by seven orders of magnitude. The IZl value for all the specimens tends to decrease with an increased cyclic number. Thus, a prolonged test must have led to the uptake of more electrolytes by the coatings. However, the rate of its uptake depended mainly on the coating systems and the concentration of UHP; the lowest rate, reflecting the gradual reduction of IZl value, was determined from the 7 wt% UHP-modified PPS/Zn·Ph coating. In contrast, the PEEK/Zn·Ph coating had the highest rate of electrolyte uptake, corresponding to a shift in IZl value from $\sim 6 \times 10^{10}$ ohm-cm² at 0 cycle to $\sim 4 \times 10^4$ ohm-cm² after 10 cycles. The data also demonstrated that the drop in IZl to low value for the UHP-free PPS/Zn·Ph coating was much faster than those for UHP-modified coatings. For the single Zn·Ph coating, after 5 cycles the IZl value remained at 5×10^2 ohm-cm², implying that there was anodic corrosion of the underlying steel. Comparing the IZl values, we ranked these coatings on a low degree of penetration of electrolyte in the following order; 7 wt% UHP- > 3 wt% UHP- > 0 wt% UHP-modified PPS/Zn·Ph > PEEK/Zn·Ph > Zn·Ph.

An important question that still remains concerned the ability of the ZnS reaction products to reduce the rate of cathodic delamination of the coating film from the Zn·Ph. Because ZnS is substantially insoluble in water and alkaline solutions, we would expect that this reaction product would suppress the delamination of polymer film caused by alkali-catalyzed dissolution of the Zn·Ph layers occurring at the cathodic reaction side, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$. Figure 5 shows the delaminated area of PEEK, and UHP-modified and unmodified PPS films from the Zn·Ph layers for 0-, 20-, 30-, 60-, and 90-cycled specimens after 8 days of cathodic tests. For PEEK/Zn·Ph/steel joint systems, the curve indicates that there is a low rate of delamination of PEEK in the first 30 cycles. However, an increase to 60 cycles resulted in the increase in the rate of delamination. As mentioned earlier, further extension to 90 cycles led to the delamination of film caused by esterification-induced decomposition of the PEEK structure at the interfaces. In contrast, the rate of delamination for the unmodified PPS joint systems was progressively reduced as a function of cyclic number; the delaminated value of ~ 1.8 mm² after 90 cycles was ~ 20 times lower than that for the control specimens. Such a dramatic reduction was due mainly to the rapid rate of in-situ conversion of the Zn·Ph layers into ZnS reaction products in the PPS-Zn·Ph interfacial regions; that is, a high conversion rate of Zn·Ph as the cycles increased caused the formation of large amounts of the ZnS reaction compound which have no effect on the cathodic reaction-caused decomposition of the interfacial intermediate layers. Thus, it is reasonable to assume that the intermediate ZnS formation, which is insoluble in alkali solution at pH ~ 13 , has a high resistivity to

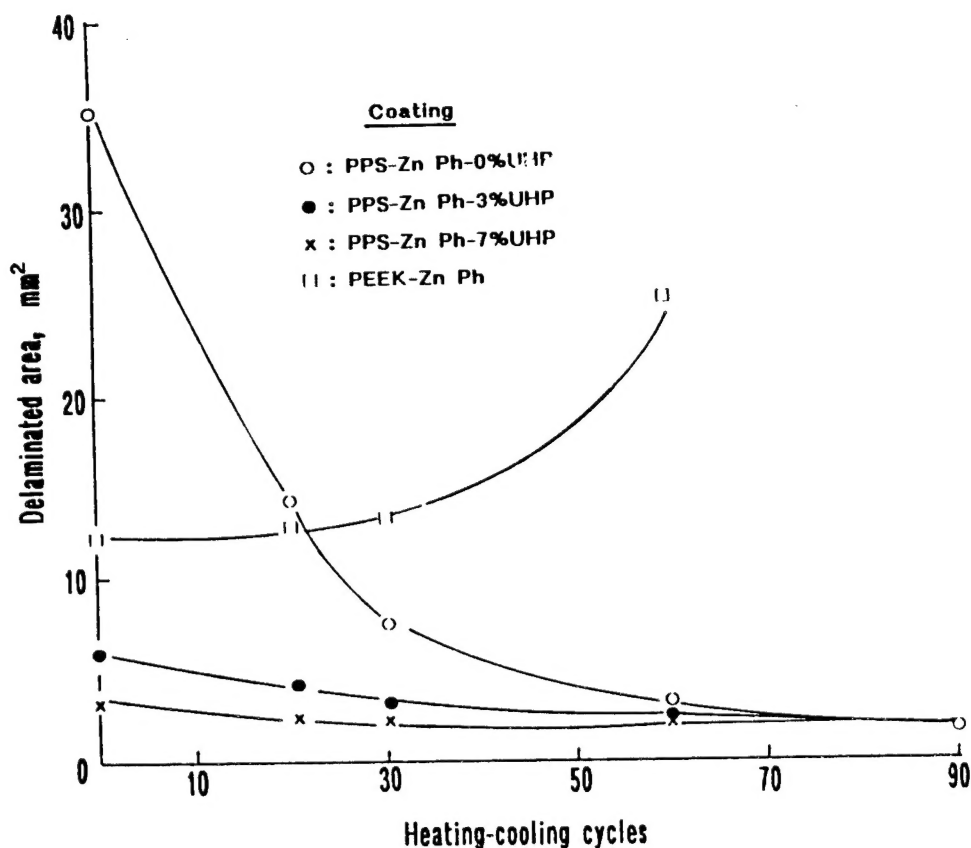


Figure 5. Rate of delamination of PEEK, and UHP-modified and unmodified PPS coating films from the substrate after cathodic tests for 8 days for polyaryl/Zn·Ph/steel joint systems as a function of heating-cooling cycles.

cathodic reaction-created alkaline environments, thereby minimizing the rate of delamination. This concept directly explains why the rate of delamination for the UHP-modified PPS systems before cycling is lower than that of unmodified specimens at 0 cycle, because of the presence of large amounts of the ZnS compound which is not susceptible to alkali-catalyzed dissolution.

Conclusion

When urea hydrogen peroxide (UHP)-modified polyphenylen sulphide (PPS) was used as the topcoat for zinc phosphate (Zn·Ph)-deposited steel substrates, the interaction between the SO₂ or SO₃ emitted from the peroxidized PPS and the Zn in Zn·Ph layers led to the formation of ZnS compounds in the interfacial boundary regions. This reaction product, in conjunction with excellent hydrothermal stability of PPS itself, played an important role in improving the PPS-to-Zn·Ph bond durability and in providing a great protection of the steel from corrosion during its exposure to a wet, harsh environment. Although the UHP-unmodified PPS was coated over the

Zn·Ph, the exposure of this coating system in autoclave at 200°C introduced the same sulfide compound into the intermediate layers; its amount progressively increased with an increased number of heating-cooling cycles. Furthermore, a specific characteristic of this reaction product was to inhibit the alkali-induced delamination of the PPS film from the substrate that was caused by the cathodic reaction, $\text{H}_2\text{O} + 1/2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$, occurring at corrosion sites in the steel, because this reaction product was insoluble at pH ~ 13. In contrast, a shortcoming of the polyphenyletheretherketone (PEEK) coating was its susceptibility of hydrothermal-catalyzed esterification. Thus, despite achieving a good bond at the PEEK-to-Zn·Ph interfaces due to the mechanical anchoring of the PEEK polymer, the esterification-induced degradation of the structure after 90 cycles caused the buckling delamination of film. As expected, PEEK coating systems which do not have any alkali-insoluble reaction products underwent the cathodic delamination because they were undermined by the alkali dissolution of Zn·Ph layers. Nevertheless, it believed that the combined layers of PPS and Zn·Ph afford great protection to steels in a harsh environment with temperatures up to 200°C.

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